

Two-dimensional spectroscopy by spectrally resolved real-time resonant coherent Raman scattering in polydiacetylene

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Abstract. Spectrally resolved real-time coherent resonant Raman scattering was observed by a 4-fs ultrashort pulse with a spectrally resolving multi-channel lock-in amplifier and was identified by a theoretical calculation. An introduced optical frequency- and vibrational time-resolved two-dimensional spectrum reveals the electronic ground-state dynamics below the absorption edge.

1. Introduction

We report the observation of spectrally resolved real-time coherent resonant Raman scattering induced by a 4-fs ultrashort-pulse laser [1] with a multi-channel lock-in amplifier, which makes it possible to detect small signals at multi-probed-wavelengths. Fig. 1 shows a schematic of a nonlinear process which is mainly used in this experiment to investigate the ground-state dynamics without coherent excitation of the excited-state dynamics. A theoretically calculated nonlinear polarization which takes the ground-state wavepackets into account reproduced fairly well the observed dynamics. It is confirmed that the ground-state vibrations play a significant role in the dynamics of the wavepacket even far below the absorption edge as well as the excited-state vibrations. In this configuration, contribution of coherent excitation of the excited-state dynamics is depressed and the ground-state dynamics will mainly contribute to observed signals.

2. Theory and Experimental

A transmittance change of the probe pulse as a function of a delay-time τ between the pump and the probe and the probed optical frequency ω is calculated by a nonlinear spectroscopy calculation [2-4] for the nonlinear process in Fig. 1 (right) as

$$\Delta T(\omega, \tau) / P(\omega) \propto (\omega_e - \omega_v) \exp(-\tau / T_4) \frac{-\Omega \sin(\omega_v \tau) + \gamma_2 \cos(\omega_v \tau)}{\Omega^2 + \gamma_2^2}$$

with $\Omega = \omega - \omega_e + \omega_v$, $\gamma_2 = 1/T_2$, $\hbar\omega_e = E_e$ and $\hbar\omega_v = E_v$ (1). $P(\omega)$,

T_2 , and T_4 , which are a pulse energy of the incident probe, an electronic transverse dephasing time constant, and an vibrational transverse dephasing time constant between vibrational states of the ground-states, respectively.

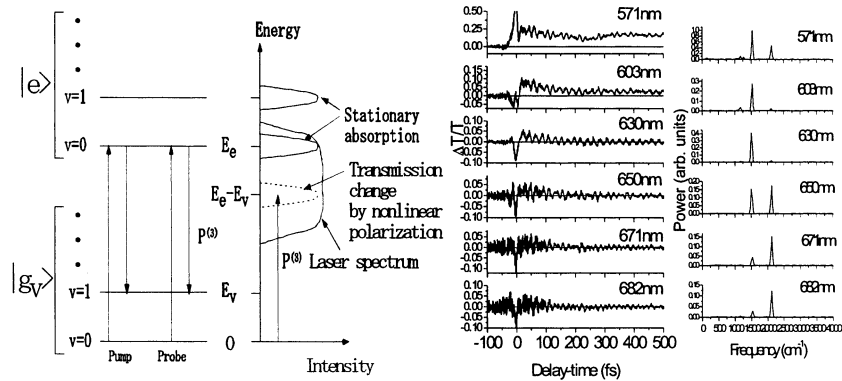


Fig. 1. Schematic diagram of the 3rd-order nonlinear processes used in this experiment (left), Real-time transmission changes (center) at 6 probed wavelengths, and FFT power spectra (right) of periodic signals of the corresponding real-time changes. $P^{(3)}$: 3rd-order nonlinear polarization, E_e : absorption energy of 0-0 transition, and E_v : vibrational energy.

From the equation, the modulated pump-probe signals by different vibrations appear at the different probed wavelengths, because a vibration with its angular frequency ω_v modulates the pump-probe signal most at $\omega = \omega_e - \omega_v$ of the probed wavelengths, which are different for different vibrations and can be located far below the absorption edge (0-0 transition in this case).

Experimentally the transmittance changes were measured by a usual pump-probe measurement with the 4-fs ultrashort-pulse laser and lock-in amplified by the multi-channel lock-in amplifier at 128 wavelengths simultaneously.

3. Result and Discussion

In Fig. 1 (center and left) typical real-time transmittance changes and corresponding Fourier transform power spectra at 6 wavelengths are selected. In the real-time transmission changes, positive transmittance changes found at 571 and 603 nm can be attributed to the bleaching of the ground-state population, which is not included in the calculation. At the other wavelengths, where neither bleaching nor photo-induced absorption was found, periodic modulations around $T/I = 0$ are observed as predicted by the Eq. Two prominent vibrational modes are found in the FT power spectra around 1500 and 2100 cm^{-1} , which can be identified with the stretching modes of carbon-carbon double- and triple-bond in the PDA main chain [5]. The relative intensities of C=C and C≡C stretching are changing gradually with the probe wavelength from 603 to 682 nm. To investigate more detailed tendency, FT power spectra at all wavelengths are shown in Fig. 2.

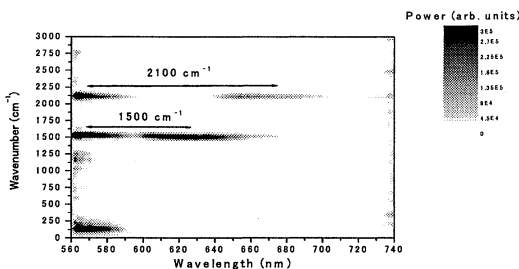


Fig. 2. FT power spectra of the periodic components of the pump-probe signal over the all probed wavelength. X, y, and z axes correspond to the probed wavelength (nm), FT frequency (cm^{-1}), and FT power (arb. units), respectively.

In Fig. 2, two broad peaks along the probed wavelength are found around 570 and 630 nm for 1516 cm^{-1} mode, and the two more signals are found around 570 and 670 nm for 2089 cm^{-1} mode. The energy separation between each peaks for the 1516 cm^{-1} mode and the 2089 cm^{-1} mode corresponds well to each vibrational energy. This fact is clearly indicated in the Eq. as the periodically modulated signal appears at $\omega = \omega_e - \omega_v$.

As predicted in the calculation, this result clearly shows the spectrally resolved real-time impulsive resonant Raman scattering of the ground-state vibrations, which had not been achieved by this time. The theoretical calculation and experiment have revealed that a pump-probe signal is affected by the ground-state dynamics at the energy far below the absorption energy. From a different point of view, in this two-dimensional diagram of Fig. 2, the spectral width of the signal (nm, horizontal axis) is related to the electronic dephasing time T_2 and the signal spectral width as a function of frequency (cm^{-1} , vertical axis) independently reflects the vibrational dephasing time T_4 . This is one of the advantages of this two-dimensional diagram, in which an electronic and vibrational dephasing times are clearly separated along the two different axes. This can be applied to a direct way to measure the transverse dephasing time between the vibrational excited-state of the electronic excited-state and the vibrational ground-state of the electronic ground-state. Whereas a stationary absorption shows the complex and broad structures by many vibration modes and broadenings, the two-dimensional diagram has resolved the overlapped vibrational spectra to each vibrational mode,

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